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Study of Effects of Adsorbed Water and Self-Assembled Monolayers on Substrate Silicon by Scanning Probe Microscopy

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1. Introduction

The electrical properties of silicon surface such as surface potential can be studied locally with high spacial resolutions using scanning probe microscopy (SPM). Obtained information is useful for surface studies including impurity distribution in silicon, adsorption of molecules, surface reactions. Among various SPM-based methodologies, scanning capacitance microscopy (SCM) has proved to be a powerful tool for 2D dopant profiling [1]. Surface potentiometry employing SPM techniques other than SCM, that is, Kelvin probe force microscopy (KFM) [2] is attractive since these can image 2D profiles of differences in the work functions of materials, which, in the case of semiconductor materials, depend on dopant type and concentration.

In order to study the effects of an adsorbed water layer and self-assembled organosilane monolayers on these scanning probe microscopies of substrate silicon, we have imaged pn structures by KFM and SCM. Here we report KFM images acquired for various surface conditions of the pn structures, and SCM images for samples with self-assembled organosilane monolayers.

2. Experiments

Silicon pn structures are prepared by the following process. Silicon wafers (n-type, resistivity: $4 \sim 6 \Omega\text{-cm}$, doped with phosphorus (P) at a density of $1 \times 10^{15}/\text{cm}^3$) were employed as a substrate on which pn-structures were fabricated through photolithography and ion implantation. By doping boron (B) with a density of $2 \times 10^{16}/\text{cm}^3$, p-type regions were formed on the n-type Si substrate. Next, arsenic (As) was highly doped with a density of $5 \times 10^{19}/\text{cm}^3$ in the regions surrounding the p- and n-type areas. Finally, the sample was oxidized and then etched with hydrofluoric acid (HF). Since the oxide layer which formed on the regions highly doped with As (i.e, the n⁺-type regions) was thicker than that on the p- and n-type regions, the n⁺-type regions became recessed from the p- and n-type regions after the oxide was removed by HF etching.

Prior to KFM imaging, the samples were

photochemically cleaned by exposing to vacuum ultraviolet (VUV) light generated from an excimer lamp [3]. This VUV-irradiation was conducted in the presence of atmospheric oxygen. Before the VUV-irradiation, the sample surface showed a water contact angle of ca. 60° due to contamination. Short-wavelength radiation in this range dissociatively excites the carbon-carbon and carbon-hydrogen bonds of organic molecules [4]. Furthermore, the light produces oxygen atoms due to photoexcitation of atmospheric oxygen molecules[5]. Consequently, organic materials are decomposed by direct photoexcitation and by the following oxidation with VUV-generated oxygen atoms. Thus, the photoirradiated samples became clean through this photochemical elimination of the surface organic contamination. The samples became covered with a thin silicon oxide (SiO_2) layer of ca. 2 nm in thickness whose surface was completely hydrophilic with its water contact angle being almost 0° . The surface was most likely terminated with OH groups. Furthermore, some of these photocleaned samples were annealed in an electric oven in order to regulate the density of surface OH group.

Surface potential images of the samples were observed by a KFM using a gold-coated Si cantilever. The cantilever was vibrated at a frequency slightly larger than its resonance frequency. An a.c. voltage of 2 V at a frequency of 25 kHz was applied between probe and sample. KFM images of the sample surface was acquired at a probe scan rate of 0.1 Hz. The measurements were conducted in air or in nitrogen

SCM observations were performed under ambient air condition for pn silicon samples with and without an organosilane self assembled monolayer (SAM). These organosilane SAMs deposited by CVD were

n-octadecyltrimethoxysilane

[ODS, $\text{H}_3\text{C}(\text{CH}_2)_{17}\text{Si}(\text{OCH}_3)_3$] and

heptadecafluoro-1,1,2,2-tetrahydro-decyl-1-trimethoxysilane

[FAS, $\text{F}_3\text{C}(\text{CF}_2)_6\text{NH}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$][1,2].

3. Experimental results of KFM measurements

In Figure 1, image (a) is a KFM image of a VUV-irradiated sample acquired in air with relative humidity (RH) about 54% at a temperature of ca. 25 °C. In image (a) there appear nine square structures of 10 μm $\times$ 10 μm consisting of the p- and n-type regions and protruding 50 nm from the surrounding n⁺-type region. However, almost no contrast can be observed in the KFM image in image (a). On the contrary, after the sample was annealed, a distinct potential contrast appeared between the p- and n-type regions even when imaging was conducted at 54% RH as shown in image (c).

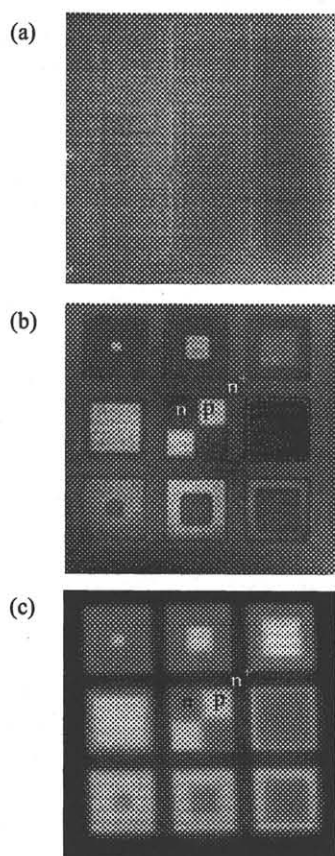


Figure 1. (a) KFM image of the sample with a hydrophilic surface showing a water contact of almost 0°. These images were acquired in air with 54% RH. (b) KFM image of the sample annealed for 3 hours in air at a temperature of 100 °C. (c) KFM image of the sample with a hydrophilic surface showing a water contact angle of almost 0°. This image was acquired in a nitrogen atmosphere with its relative humidity being less than 0.6%.

Since the adsorbed water shields the surface potential in KFM imaging, it is expected to depend not only on the surface hydrophobicity of sample surfaces but also on atmospheric conditions for KFM imaging, particularly humidity. Indeed, as demonstrated in Fig. 1(c), the pn-structures covered with a hydrophilic oxide, which were not observable under the humid atmosphere as shown in Fig. 1(a), are clearly imaged by KFM in a low-humidity atmosphere.

4. Experimental results of SCM measurements

Clear contrasts in SCM images were obtained for samples with no SAM. However, samples with a SAM showed less contrast as shown in Fig. 2. As expected, the signal of N⁺ region was not affected by the monolayers. The contrast degradation was caused by the decrease of the SCM signal of n-type region in the case of ODS. In the case of FAS, the both SCM signals of p and n type regions became almost zero, by which the contrast became very faint in this case.

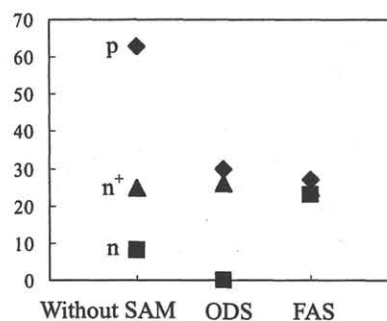


Fig. 2 SCM signals at p, n, n⁺ regions, which make contrasts in SCM images, for the pn silicon samples without and with SAM.

5. Conclusions

The surface potential contrast between the p- and n-type regions depended on the hydrophobicity of the oxide surface when KFM imaging was conducted in humid air. Since samples with less adsorbed water on their surface showed greater potential contrast, the contrast degradation in KFM imaging is attributed to a shielding effect of the adsorbed water layer. The contrast in SCM imaging became smaller by applying organosilane SAM on the ample surface of silicon pn structure. The effects of the monolayer were different on different p, n and n⁺ silicon regions.

Acknowledgments

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